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Note

Chromatographic study of optical resolution

VII*. Directional ion-association model for the optical resolution of *cis*-[Co(O)₂(N)₄]⁺ type of complexes by the antimony *d*-tartrate ion

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For the optical resolution of octahedral metal complexes by ion-exchange chromatography, the antimony *d*-tartrate anion, [Sb₂(*d*-tart)₂]²⁻, is known to be a very effective eluent. Recently, we have proposed^{2,3} the L-J model as a stereoselective ion-association mode between a metal complex cation and the [Sb₂(*d*-tart)₂]²⁻ anion. The model has been shown to explain nicely the elution behaviour of tripositive complexes of cobalt(III). Because tripositive cobalt(III) complexes contain only electrically neutral ligands, there is no charge localization in such complexes. In contrast, significant charge localization is expected for dipositive or monopositive cobalt(III) complex cations⁴, because these complex cations contain anionic ligands. Therefore, when these cations are chromatographed by [Sb₂(*d*-tart)₂]²⁻, the position where the L-shaped channel^{2,3} is situated seems to be very important. In this paper, some monopositive cobalt(III) complexes are subjected to ion-exchange chromatography by [Sb₂(*d*-tart)₂]²⁻, and the result is interpreted in terms of the L-J model with directional ion-association taken into consideration.

EXPERIMENTAL

The two geometrical isomers, *cis*(O),*cis*(N),*cis*(NH₃) and *cis*(O),*trans*(N),*cis*(NH₃), of [Co(gly)₂(NH₃)₂]⁺, and the two geometrical isomers, C₁-*cis*(O) and C₂-*cis*(O), of [Co(gly)₂(en)]⁺ were prepared according to the methods of Kobayashi and Shibata⁵ and Dabrowiak and Cooke⁶, respectively, where gly stands for the glycinate ion and en for ethylenediamine. SP-Sephadex C-25 resin was packed in a 31.5 cm × 6.5 mm I.D. column. The sample solution containing Blue Dextran 2000, which was used as a marker for the void volume measurement of the column, was charged on the column and was eluted with 0.1 M aqueous solution of K₂[Sb₂(*d*-tart)₂] at a constant rate of 0.33 ml/min. The adjusted retention volumes were measured by a spectrophotometer at a wavelength of the first *d-d* transition region.

* Part VI: ref. 1.

RESULTS AND DISCUSSION

The L-shaped channel was defined in the previous papers^{2,3} as the L-shaped opening between chelate rings, and the J-shaped channel as the mirror image of the L-shaped channel. The optically active $[\text{Sb}_2(d\text{-tart})_2]^{2-}$ anion can associate intimately with that enantiomer of a metal complex cation that has the L-shaped channel, but cannot associate closely with the enantiomer that has only the J-shaped channel. If we suppose that there is no charge localization in metal complexes, as in tripositive cobalt(III) complexes, the separation factor when $[\text{Sb}_2(d\text{-tart})_2]^{2-}$ is used as an eluent increases with an increase in the difference in the number of L-shaped channels between a pair of enantiomers. On the other hand, in the optical resolution of metal complexes for which charge localization appears to be significant, the position, not the number, of the L-shaped channels in a complex cation may play an important role. In the case of the $\text{cis-}[\text{Co}(\text{O})_2(\text{N})_4]^+$ type of complex, because two oxygen donor atoms carry negative charges, the eluent anion will associate with the complex cation along the direction of the twofold axis and from the side opposite the two oxygen donor atoms. As shown in Fig. 1a, the $\text{cis-}[\text{Co}(\text{O})_2(\text{N})_4]^+$ type of complex has five kinds of edge of an octahedron, which are different stereochemically. Here, rank 1 is the best position to associate with an anion electrostatically, and the ease of access of an anion toward the complex cation decreases from the edge of rank 2 to the edge of rank 5. The L-shaped channel is represented as one edge of an octahedron (Fig. 1b). In other words, there are five stereochemically different kinds of L-shaped channel in the $\text{cis-}[\text{Co}(\text{O})_2(\text{N})_4]^+$ type complexes.

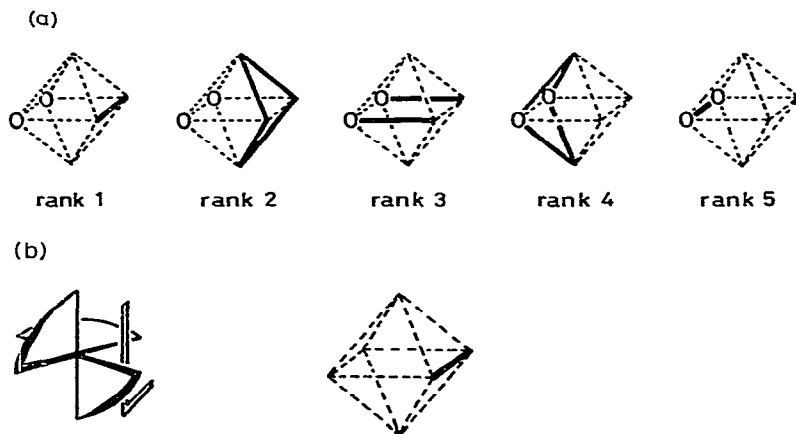


Fig. 1. (a) Stereochemically different edges (solid line) of the $\text{cis-}[\text{Co}(\text{O})_2(\text{N})_4]^+$ type of complex. (b) The L-shaped channel is represented as one edge (solid line) of an octahedron. See ref. 2.

The number and position of the L- and J-shaped channels of the Δ enantiomer of the complexes examined in this paper are listed in Table I. The term "LJ" in Table I stands for the opening that can be regarded as both the L- and J-shaped channels. Because the Δ enantiomers of complexes 3 and 4 have only the L-shaped channels, the Δ enantiomers of these complexes may be expected to be eluted first. Further, because complex 3 has L-shaped channels of higher rank than complex 4 does, the

TABLE I

THE NUMBER AND POSITION (EXPRESSED IN RANK OF FIG.1(a)) OF THE L- AND J-SHAPED CHANNELS OF THE Δ ENANTIOMERS

"LJ" stands for the opening that can be regarded as both the L- and J-shaped channels.

| Complex | Rank 1 | Rank 2 | Rank 3 | Rank 4 | Rank 5 |
|---|--------|--------------------|--------|--------|--------|
| 1 $cis(O),cis(N),cis(NH_3)-[Co(gly)_2(NH_3)_2]^+$ | 1 LJ | 2 L 1 J 1 LJ | 1 J | 1 LJ | 1 L |
| 2 $cis(O),trans(N),cis(NH_3)-[Co(gly)_2(NH_3)_2]^+$ | 1 LJ | 2 J 2 LJ | 2 L | 2 L | — |
| 3 $C_1-cis(O)-[Co(gly)_2(en)]^+$ | 1 L | 2 L | — | — | 1 L |
| 4 $C_2-cis(O)-[Co(gly)_2(en)]^+$ | — | — | 2 L | 2 L | — |

separation factor of complex 3 may be better than that of complex 4. For complex 1, because the Δ enantiomer has two L-shaped channels and one J-shaped channel, both of rank 2, it is expected that the Δ enantiomer is eluted first. In contrast, for complex 2, because the Δ enantiomer has two L-shaped channels, the Δ enantiomer is expected to be eluted first. Thus, the present model predicts that the absolute configuration of the first eluted enantiomer is Δ for $cis(O),cis(N),cis(NH_3)-[Co(gly)_2(NH_3)_2]^+$, whereas it is Δ for $cis(O),trans(N),cis(NH_3)-[Co(gly)_2(NH_3)_2]^+$. Moreover, it may be predicted that the separation factor of complex 2 is better than that of complex 1.

The results are shown in Table II. Although the absolute configurations of complexes 1 and 2 have not been established by single crystal X-ray analysis, the absolute configuration of the first eluted enantiomer of complex 1 is considered to be Δ because the sign of the dominant circular dichroism (CD) band is plus, with a maximum at 529 nm, and that of complex 2 may be Δ because the sign of the dominant CD band is minus, with a maximum at 520 nm. The absolute configuration of the first eluted enantiomers of complexes 3 and 4 has been assigned as Δ^o . These deductions of the absolute configuration of the first eluted enantiomers are in line with the prediction based on the L-J model described above.

TABLE II

THE RETENTION VOLUMES AND THE SEPARATION FACTORS OF COMPLEXES 1-4 WHEN CHROMATOGRAPHED WITH 0.1 M $K_2[Sb_2(d-tart)_2]$

| Complex | Retention volume (ml) | Separation factor |
|---|--|-------------------|
| 1 $cis(O),cis(N),cis(NH_3)-[Co(gly)_2(NH_3)_2]^+$ | 13.83 | —* |
| 2 $cis(O),trans(N),cis(NH_3)-[Co(gly)_2(NH_3)_2]^+$ | 12.20 (Δ) 14.03 (Δ) | 1.150 |
| 3 $C_1-cis(O)-[Co(gly)_2(en)]^+$ | 13.29 (Δ) 15.75 (Δ) | 1.185 |
| 4 $C_2-cis(O)-[Co(gly)_2(en)]^+$ | 15.79 | —* |

* Separation factors could not be obtained because of partial resolution.

Let us compare the retention volumes of complexes 1 and 2. The average number of L-shaped channels of the *A* and *Δ* enantiomers of complex 1 is one of rank 1 and 2.5 of rank 2, whereas for complex 2 the number of L-shaped channels of the *Δ* enantiomer is one of rank 1 and four of rank 2 and that of the *A* enantiomer is one of rank 1 and two of rank 2. Complex 2 was optically resolved completely, and the retention volume of complex 1 is closer to that of the *A* enantiomer of complex 2 than that of the *Δ* enantiomer of complex 2. This result might also support the validity of the reasoning that was based on the L-J model and took directional ion-association into consideration.

The absolute configuration of the first eluted enantiomers is *A* for complexes 3 and 4, and complete resolution was attained for complex 3. The results are in line with the prediction described above. Moreover, the fact that the retention volume of complex 4 is almost equal to that of the *Δ* enantiomer of complex 3 may support the L-J model with directional ion-association, because the *Δ* enantiomer of complex 3 and both enantiomers of complex 4 have no L-shaped channel of rank 1 and rank 2.

Therefore, it is concluded that if directional ion-association is considered for complexes having charge localization, the elution order and the degree of separation when eluted with $[\text{Sb}_2(d\text{-tart})_2]^{2-}$ are reasonably predicted according to the L-J model.

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